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As part of an investigation into the effect of organic compounds on the retardation of the hydration of portland cement, it has been observed that the most effective retarders also inhibit the precipitation of calcium hydroxide from aqueous solution. This effect could indicate the mechanism of action of these compounds.

The principal chemical reactions occurring in the setting and hydration of cement are

$$C_3A + H + C\bar{S} \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}$$

$$C_3S + H \rightarrow C\text{–}S\text{–}H + CH$$

where C = CaO, S = SiO_2, A = Al_2O_3, H = H_2O and $\bar{S}$ = SO_3.

Setting is the outward mechanical manifestation of the growth and interlocking of C–S–H crystals [1], after the end of the dormant period, and is accompanied by the precipitation of crystals of CH, calcium hydroxide, from the aqueous solution, which is at this stage considerably supersaturated [2]. Regardless of whether the precipitation of CH precedes the onset of C–S–H formation [3], or vice versa [4], it is evident that nucleation and growth of calcium hydroxide crystals must take place in order for hydration to continue. That organic retarding admixtures may adsorb on to calcium hydroxide nuclei and prevent their growth appears to have been first suggested by Greening [5], and subsequently considered likely by other workers [6, 7], but no confirmation has been reported. This letter reports results obtained with a simple spot test designed to examine the validity of the nucleation hypothesis.

A 0.1 M solution of $CaCl_2$ (5 ml) was mixed with 1 M NaOH (1 ml) in a centrifuge tube. This produced 6 ml of a solution 0.083 M in Ca^{2+} and 0.167 M in OH^-, about 3.5 times the saturation solubility of $Ca(OH)_2$ in water at 20° C. For comparison the concentrations of Ca^{2+} and OH^- in the aqueous phase in fresh cement paste reach a maximum of about double the saturation concentration at the end of the dormant period, so that the experimental conditions used here are slightly more severe. As expected, a heavy precipitate of calcium hydroxide was formed as soon as the solutions were mixed.

When organic compounds were dissolved in the calcium chloride solution the time taken for the precipitate to form increased markedly and the amount produced was less. A series of precipitation tests carried out using a standard quantity of organic compounds gave the rank order in Table I. An aqueous solution (0.15 ml) containing 0.1 M of the compound shown was added to the $CaCl_2$ solution and the precipitation index (scale 0 to 10) in the table was derived from a subjective assessment of two criteria – the time to appearance of precipitate (which varied up to several hours after mixing) and the amount of precipitate. Thus, zero represents a solution which remained clear for at least 48 h and 10 represents the immediate production of a heavy precipitate. The amount of precipitate formed was estimated by measuring the volume of sediment obtained upon centrifugation.

TABLE I Precipitation and retardation indices for the compounds tested

No.	Compound	Precipitation Index	Retardation Index	Reference
1	Sucrose	0.1	3	[8]
			5	[10]
			4	[11]
2	Mannose	1	2	[9]
3	Raffinose	1	4	[8]
			4	[11]
4	Glucose	2	3	[9]
			3	[10]
			2	[11]
5	Arabinose	3	3	[9]
			1	[11]
6	Galactose	3	3	[9]
7	Catechol	3	2	[8]
8	Quinol	4	1	[7]
9	EDTA	4	2	[6]
10	Orcinol	5	1	[7]
11	Phenol	5	0	[8]
12	Pyruvic acid	5	1	[8]
13	Formic acid	5	0	[8]
14	Cellobiose	5	2	[6]
			2	[11]
15	Lactic acid	5	0	[8]
16	Glycollic acid	6	0	[8]
17	Trehalose	7	0	[8]
			0	[10]
18	Lactose	7	1	[8]
			2	[11]
19	Control	10	0	

The organic compounds tested cover a wide range of retarding effects and Table I gives a retardation index compiled from data in the literature as follows. Wilding *et al.* [8] plotted the maximum rate of heat evolution obtained in a conduction calorimeter against the reciprocal of the time to that maximum. Most of their results lie near a straight line passing through the origin (shown schematically in Fig. 1) where retardation increases towards the origin. This region of retardation was then arbitrarily scaled into five equal sized zones and the retardation index assigned to each compound according to its position

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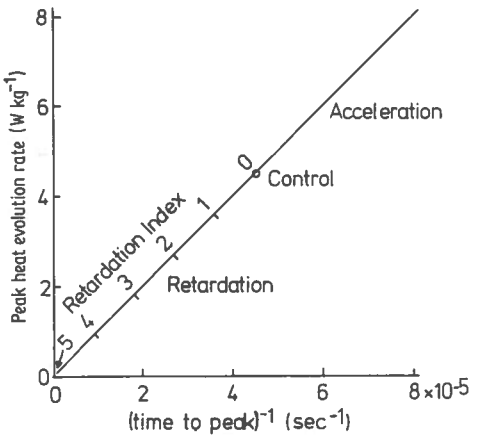

Figure 1 Derivation of the retarding index for organic compounds (based on classification by Wilding *et al.* [8]).

along the line. This procedure locates the index values (1 – slight retardation; 5 – severe retardation) at times to the peak of 1.20, 1.5, 2.2, 5.1 and ∞ times the control value. In contrast Mouton [9] and Bruere [10] reported times to initial and final set and Previte [11] reported the extension of the dormant period determined by conduction calorimetry. The results of these three workers were all scaled in the same way to give the index value, which shows acceptable agreement for any particular compound.

Fig. 2 shows that there is a negative exponential correlation between retarding index and precipitation index with a correlation coefficient between log (precipitation index) and the retarding index of -0.765 which is significant at the 1% level (26 results). In view of the subjective nature of the data and their derivation from diverse sources this significant correlation is a finding of major importance and suggests that the two phenomena are related.

The action of the organic compounds on the nucleation and precipitation of calcium hydroxide from aqueous solution, and by analogy in hydrating cement, could take one of two forms. The organic compound may chelate Ca^{2+} ions, reducing their activity and hence the apparent supersaturation of the solution with respect to $Ca(OH)_2$ as they form and poison their growth. The fact that EDTA is a much stronger calcium chelating agent than most of the

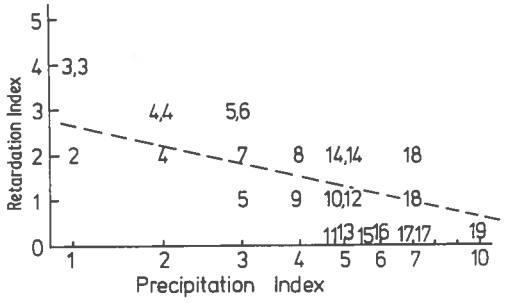

Figure 2 The relationship between retardation index and precipitation index. Numbers denote the compounds listed in Table I.

sugars tested in this work [6] but has less effect on the precipitation implies that the former mechanism is incorrect and confirms the lack of correlation between calcium complexing ability of sugars and their retarding ability [6]. Further, Thomas and Birchall suggest that sugar–calcium salts formed in alkaline solution can adsorb on to calcium hydroxide and although such behaviour is difficult to observe directly, much simpler non-labile organic compounds have been shown to adsorb [7]. A further point in favour of the nuclei poisoning model is that the precipitates formed in the presence of compounds with the highest retardation index were finer grained, tending towards colloidal dimensions, than the control and low-retardation precipitates. The model also accounts for the high Ca^{2+} concentrations seen in solution in retarded hydrating cement.

Evidence is thus accumulating in favour of a model for the mechanism of retardation of the hydration of Portland cement based on the adsorption of the organic species onto nuclei or calcium hydroxide whose growth is thus poisoned. It should be pointed out that C–S–H gel also grows in hydrating cement and it is possible that the same poisoning effect applies to that material. The possibility of chelation being the dominant mechanism in other cements, e.g. aluminous and magnesium phosphate, should not, of course, be ruled out.

In conclusion, the observation that organic compounds which retard the hydration of cement also delay the precipitation of calcium hydroxide from aqueous solution is evidence for a mechanism of retardation based on the poisoning by the organic compound of the growth of calcium hydroxide nuclei in hydrating cement.

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